Analytical Chemistry
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Module 10
Lecture No 48
Electrochemical Methods 2 (Contd)

Hello and welcome to this class again where we are still continuing the electrochemical methods and now we will talk the effect of the current, effect of the current on solutions and these solutions are your electro active solutions, so effect of the current will see how this can be seen because these solutions are there in some electrochemical cells. So we want to see the effect of current on solutions and these solutions are nothing but your analyte or the analytes and electrochemical cell is there and why we are looking for that particular electrochemical cell is that the corresponding E0 value that means the corresponding cell potential.

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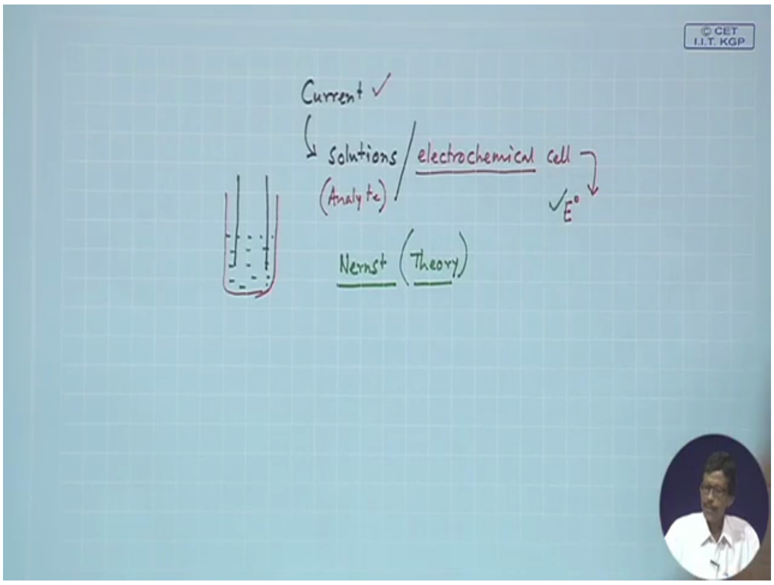

So once we look at the corresponding cell potential we must have some idea about the corresponding passage of current or the cell is producing some amount of current, so the net current in an electrochemical cell what we have defined earlier also the one is your galvanic cell and another is your electrochemical cell. So the net current in an electrochemical cell that which can be measured potential across the two electrodes so if you have a cell or any simple beaker and we have two electrodes inserted within the solution of this and this particular solution what you can have.

So electrodes are there and how we measure that means the measured potential across the two electrodes so it is at some point cannot be the simple difference between the two electrodes as calculated from some equation we know which is your Nernst equation. So Nernst equation was applicable to calculate out this E0 value and now we will see whether we can directly or theoretically that means it is the theory which can tell us that ok we can use Nernst equation to calculate out this particular current as well as the potential for any effect of current on a solution

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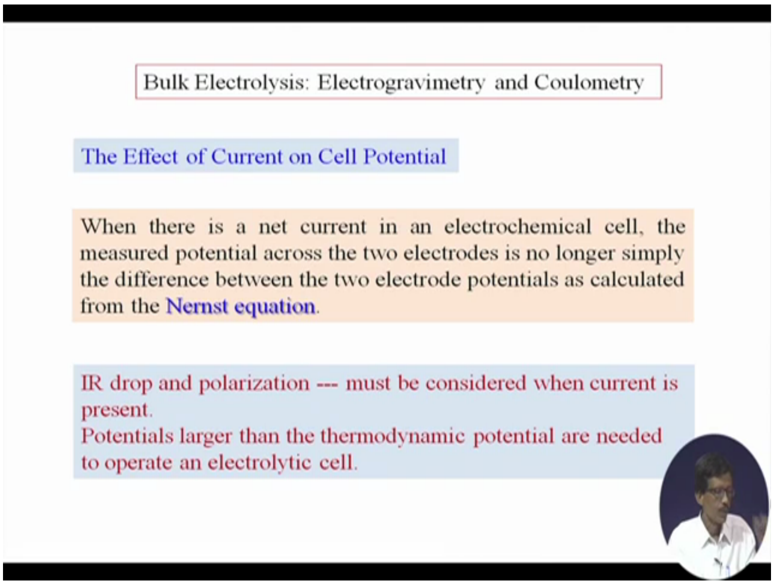

Bulk Electrolysis: Electrogravimetry and Coulometry

The Effect of Current on Cell Potential

When there is a net current in an electrochemical cell, the measured potential across the two electrodes is no longer simply the difference between the two electrode potentials as calculated from the Nernst equation.

IR drop and polarization --- must be considered when current is present.
Potentials larger than the thermodynamic potential are needed to operate an electrolytic cell.

So now we will see this particular one in terms of bulk electrolysis. So we just basically go for that means we will apply current to the solution containing the analyte to clearly see the corresponding effect of that particular current and which is being introduced directly through the electrodes. So electrodes are there, electrodes materials are important so basically the bulk electrolysis that means the entire electrolysis of the solution is not that the some electron transfer is taking place on the surface of the electrode or some other electroactive material.

So we will be getting two techniques basically two methods or two processes, one will be called as Electrogravimetry and the other is the Coulometry that means Coulometry as I told you that is the corresponding amount of current or the electric charge which is passed through the solution but electrogravimetry is by owing we do something because the gravimetric estimation we know earlier. Now electricity is passed and some changes is there and the change of the mass in terms of the corresponding depletion from the solution or deposition on the electrode can be measured for this particular type of technique.

So we will see the effect of current on cell potential that we are just looking for and when there is no net current in the electrochemical cell, the measured potential across the two electrodes is no longer as I told you just now is the difference between the two electrodes potential as we calculate out from the theoretically predicted equation which is your Nernst equation. So what we should see that once we have the Nernst equation we have IR drop and polarisation. So it should be considered that means the IR drop and polarization, so two things are coming into the picture and these two things we will now discuss that when Nernst theory or Nernst equation we are not able to that means some modification.

We should get some modification of that equation so this modification in terms of the IR drop and second is polarization because we are talking about the corresponding amount of current so this basically we have to operate electrochemical cell and how we can operate a particular electrochemical cell such that what potential we should apply and the potentials larger or smaller than that of the thermodynamic potential what we can calculate using the Nernst equation.

So IR drop and polarization both we should consider when there is a current that means current is there and current is passing through the electrodes and potentials larger than thermodynamics potentials are need to operate an electrolytic cell, so when we have IR drop and polarization. So these are the two basically reducing things that which can also go against the corresponding potential values so we have to use a higher potential value than the thermodynamics potential value such that we get some very small amount of current in the cell otherwise, we will not get that particular current.

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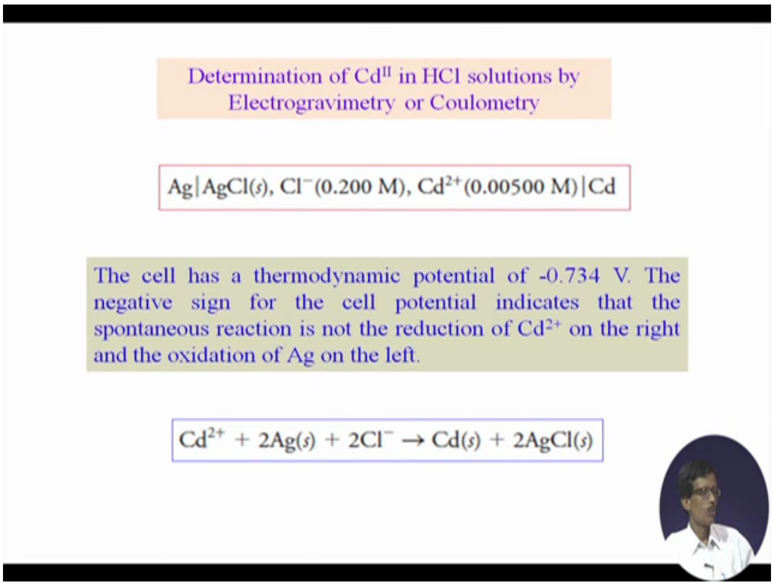

Determination of Cd^{II} in HCl solutions by Electrogravimetry or Coulometry

$Ag|AgCl(s), Cl^-(0.200\ M), Cd^{2+}(0.00500\ M)|Cd$

The cell has a thermodynamic potential of -0.734 V. The negative sign for the cell potential indicates that the spontaneous reaction is not the reduction of Cd^{2+} on the right and the oxidation of Ag on the left.

$Cd^{2+} + 2Ag(s) + 2Cl^- \rightarrow Cd(s) + 2AgCl(s)$

So one such example is that electrochemical cell we use for the determination of cadmium in HCL solutions by electrogravimetry or coulometry, so we should know the corresponding cell arrangement, so what should be the corresponding cell arrangement, that means we have to use this for the reduction of cadmium 2 + which having some concentration and a cadmium wire or cadmium plate can be your electrode. So what we get over there from this particular determination that we have a cell so this is on the right hand side you have the cadmium is getting reduced to cadmium metal.

So what we get with a certain concentration of that cadmium solution and on the left hand you have the corresponding reference electrodes which is based on silver-silver chloride electrodes having a particular chloride concentration of 0.2 molar. So this particular cell has a thermodynamic potential which we can measure as – 0.73 volt. So if we consider that this negative sign of the cell potential indicates that there is no spontaneous reaction for the reduction of cadmium 2 + on the right and oxidation of silver on the left because the cell convention we know that on the right you have the reduction and on the left you have the corresponding oxidation.

So whether if it is coupled at all with that of our standard silver-silver chloride reference electrode whether we get a corresponding process which is spontaneous for the reaction where you get that the cadmium will be reduced to cadmium metal or the metallic cadmium on the electrodes surface and silver will be oxidized to silver chloride in presence of certain amount of chloride already present in the solution. So that basically gives us some ideas that whether we will be able to use this for the corresponding determination as well as quantitative estimation of cadmium 2 + in the solution.

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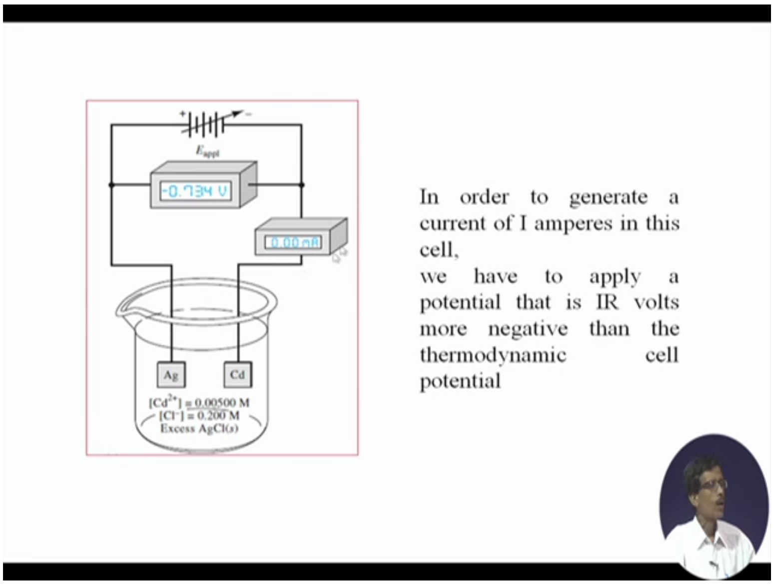

In order to generate a current of I amperes in this cell,
we have to apply a potential that is IR volts more negative than the thermodynamic cell potential

So what we see that you have a corresponding cell and you get that particular cell as silver-silver chloride electrode on the left and cadmium on the right and as I told you the corresponding values. So if you have this and if the cell is there, we will try to measure the potential which is there as – 0.73 volt as calculated, but if we see in the circuit that the corresponding ammeter if it is there which can find the corresponding amount of current which is passing through this circuit is zero.

So is 0.00 milliampere is the current so no net current is passing through the solution and there is something that we are not getting that particular thing that means this is the corresponding E applied and E applied potential is similar to that of your potential what is measured from there, but due to that particular ohmic potential ohmic potential is will see that is multiplication of the corresponding current and the resistance.

So in order to generate a current of I ampere in the cell because here we see that no more is there so if we want to get some amount of current to be seen to be recorded from this solution what we have to do we have apply and a potential that is IR volts more negative than the thermodynamics cell potential, that means we have a ohmic potential and the ohmic potential have to be added to that cell potential, so thermodynamic cell potential was – 0.73 volt

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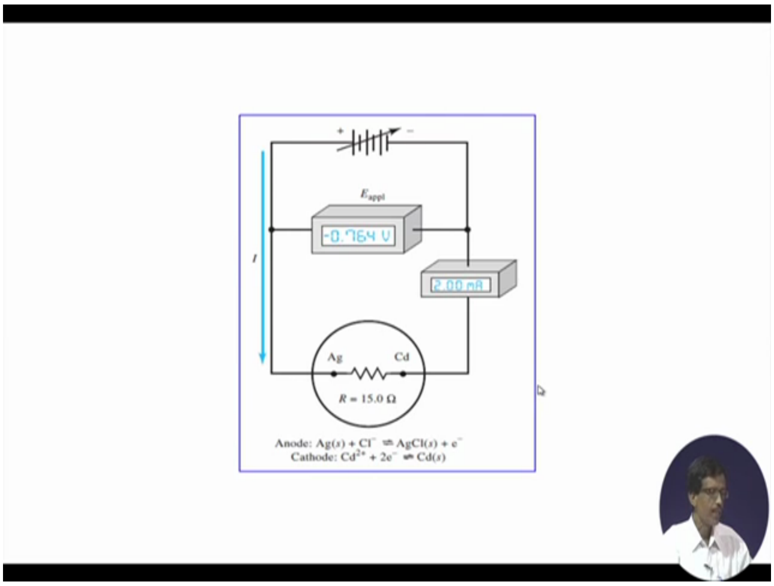

Anode: $Ag(s) + Cl^- \rightleftharpoons AgCl(s) + e^-$
Cathode: $Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$

Now we will see what sort of resistance we have that I we know that I once we know the current how much current we can pass through it and the resistance, the resistance of the cell we should know. So if the cell of the resistance is known and then we can find out the corresponding applied potential beyond the thermodynamic potential value so this basically gives us these things that means if you have a R value of 15 ohm, so that is the ohmic potential or the IR drop of the cell.

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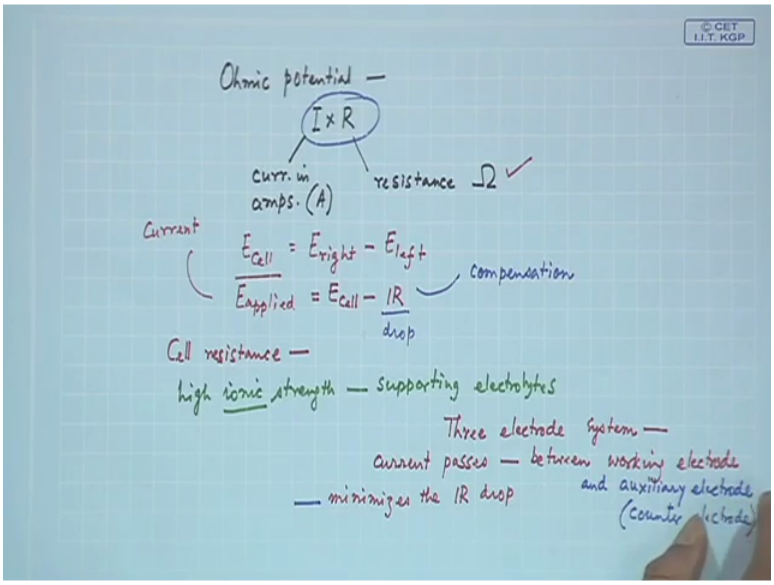

Ohmic potential –

$\boxed{I \times R}$

curr. in amps. (A)

resistance Ω ✓

Current

$E_{Cell} = E_{right} - E_{left}$

$E_{Applied} = E_{Cell} - \underline{IR}$ — compensation

drop

Cell resistance –

high ionic strength – supporting electrolytes

Three electrode system –

current passes – between working electrode and auxiliary electrode (counter electrode)

– minimizes the IR drop

So if we have a corresponding potential value in that way, so we get basically from there, the ohmic potential values which basically resisting the flow of charge which is nothing but a product of I and R. So IR drop of the cell where I is the corresponding current in amperes in amps, it can be milliamperes also and resistance R in unit of ohm. So what we get now that we have that particular intension that how we measure the corresponding E cell as we know in all other previous cases that E cell was E right – E left.

Now we have generate a current of I amperes in the cell so we must apply some potential which is higher than that of the potential required for the correspond cell. So now E applied what we should apply such that we get some current in the cell. We require some current within the cell so E applied will be therefore that you can have this particular thing that E applied will be E cell now this E cell – your IR drop of the cell. So we add up this IR drop in the cell and we can calculate it out how much you have the IR drop.

So we basically this we will find out and when we discuss about the cyclic voltammetry measurement is another electrochemical technique, so this particular one that means we can consider as IR compensation and automatically the most modern instruments the contemporary instruments which is available in the market for the recording of cyclic voltammetry measurements. You can have some the corresponding adjustment in terms of their IR drop. So IR drop is the most important factor over there to get some current over this particular cell.

So if you have some 15 ohmic current resistance within the cell between these two electrodes of silver and cadmium so this is the resistor we have been shown. So cell itself has a resistance, so what we get we want to have a flow of current of I such that you can have 2 millimampere current such that you apply potential will change, so it is changing from – 0.7344 to – 0.764 volts so these increase in this corresponding E applied. The applied voltage is due to the corresponding generated cell resistance and we consider this as the corresponding drop in the method.

What we use for your electrogavimetric technique so this particular IR drop so we considering is as the corresponding IR drop. How to reduce this particular IR drop, so in a particular cell when we use and we have seen that a typical mechanism will apply goes if the IR drop is very much your E applied will be above much more above than that of your E cell. So what we should do. we should have some idea about the corresponding cell resistance so how to reduce the cell resistance that resistance what we are seeing how to reduce this particular cell resistance that is an important thing.

So if in the solution we have species or the salt which can give rise to high ionic strength or we add something sometime we will be seeing that we will add supporting electrolytes so these supporting electrolytes having high ionic strength can reduce the cell resistance, so IR drop will be less. As a result we have something that we go for instead of two electrode system because in cyclic voltammetry measurement also we will find a three electrode system and that is very much useful for the cell it can be considered as a three electrode cell and there the current what we have just seen that 2 milliampere current so their basically the entire current is passes between working electrode.

So which is electrode where we just go for its nature that means is a cathode or anode, working electrode and auxiliary electrode will put some, auxiliary electrode. So the entire current is passing through working electrode and we are bringing something as your auxiliary electrode and this auxiliary electrode is also known as counter electrode. That means your reference electrode is not hampered much, the current is not passing through the reference electrode because this is utilized again one technique is the maintaining the strength of high ionic strength and also this particular introduction of auxiliary electrode which is a counter electrode and which again minimizes your IR drop.

So it minimizes the IR drop, so that basically gives us some important ideas to ask that how we can use for this and what are these ohmic potential and how these potential can be compensated. So for this electrogavimetric method what will be see that if we go for some measurement where you have the control potential that means potentials you have to control for these electrogavimetric measurements. So like that of our IR drop another one the second one what we are considering is your polarization effect, polarization effect.

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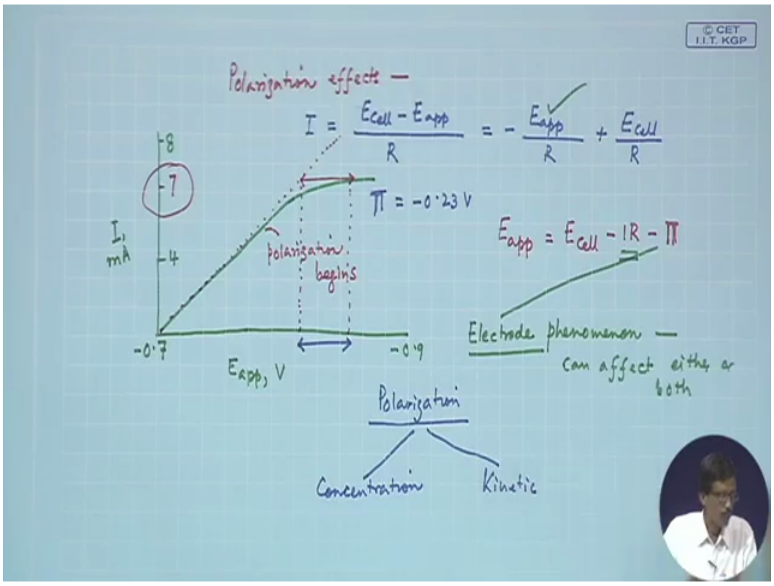

Polarization effect –

$$I = \frac{E_{cell} - E_{app}}{R} = -\frac{E_{app}}{R} + \frac{E_{cell}}{R}$$

$\pi = -0.23\ V$

$E_{app} = E_{cell} - IR - \pi$

Electrode phenomenon – can affect either or both

Polarization

- Concentration
- Kinetic

So as we have seen just now that E applied is equal to E cell – IR in electrochemical cell. Now if we see that if we want to plot the corresponding amount of current what we will be getting that means I and that we get from that the total is E cell – E app that means the applied potential divided by your resistance R is equal to therefore – E app taking this first divided by R + E cell divided by R. Now what we want to do we want to plot it to see the thing that means how the corresponding dependence that means the variation we can see. If we try to monitor the current in milliampere and the corresponding E app, this E app will be plotting so therefore E app is there. So E app in volt so we will starting from 0.7 volt to – 0.9 volts and current is basically 4 ampere to 8 ampere.

So what we see in this particular case that means I is plotted against I is plotted against E app this, so we will see that means that what we will get that the corresponding magnitude of this for your this R value how it is changing, so is basically up to certain point you have the linearity and then it is deviating that means when the current is high, (())(21:16) 4 and it is 8 milliampere.

So at this level basically when the current is high and if we because the you have the corresponding linear function you can have, so the deviation from this linearity can be extrapolated like this and at say here you can have the corresponding value of these of 7 millivolts milliampere sorry 7 milliampere so at this 7 milliampere how much deviation we get for this magnitude, this magnitude at 7 we get so this particular magnitude so here that corresponding one where it is deviating that means this polarization behaviour or the polarization effect is starting at this point.

So your polarization begins at this particular point and now we get the corresponding polarization effect which is Pie that capital Pie is equal to – 0.23 volt this particular magnitude, this particular magnitude of this potential we get, that means this basically gives us the idea about the corresponding one because this dotted one is the corresponding theoretical curve where you do not have any polarization that means no polarization line so this is your no polarization line and this is giving you the corresponding degree of polarization.

So at this point when we tried to gather a value of this 0.7 so to achieve a current of 0.7 milliampere in the electrolytic cell, we have to face this particular polarization effect in this case, so your equation for that what we are looking at, so E app is therefore changing which will be your E cell – IR drop the ohmic potential we have discussed earlier + your Pie value that means your polarization effect. So this polarization effect as we have seen that this IR the IR drop or the ohmic potential value is due to the solution of the corresponding electrode cell system.

But this particular one the polarization is the corresponding value for your electrodes, so this basically this is your the Pie is your electrode phenomena so it can affect either or the both can affect either the cathode or the anode or both, either or both the electrodes, so this polarization effect can have some interesting observation to get that means you can have this polarization effect of two types.

One is the corresponding concentration polarization and other is the kinetic polarization so way we all know that when we talk in terms of the electrode potential we have the thermodynamics electrode potential but you can also have some kinetic effect the kinetic kinetics for the electron transfer reaction. How fast and how slow is for your electron transfer reaction whether you are talking in terms of the oxidation or the reduction reaction so you have the concentration polarization as well as the kinetic polarization.

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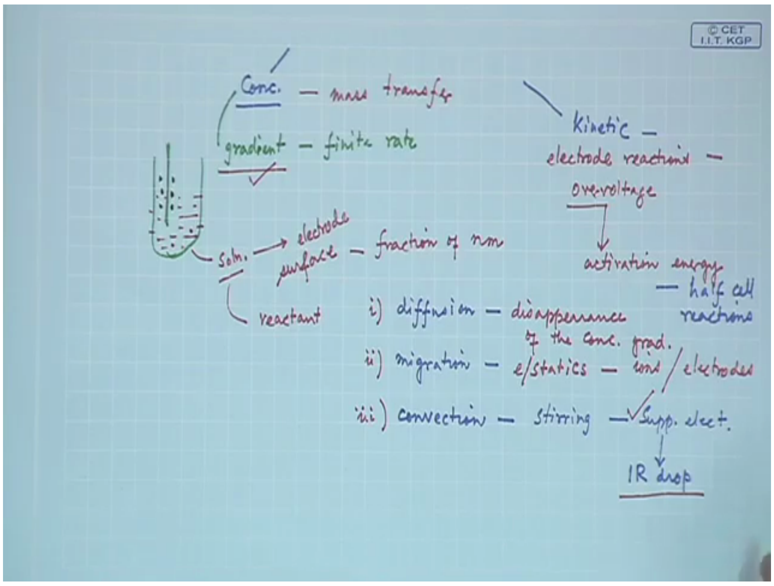

So when we talk in terms of the concentration this is very important aspect at this point to understand since we have a variable concentration of the solutions, so you have some when you have a concentration definitely we must have the concentration gradient in the solution and that concentration gradient is very important in terms of a rate of mass transfer.

So there will be finite rate for the mass transfer because what we see that if you have the cell, an electrode is dipped inside and that electrode you have some say if you have the corresponding electrode responsible for the reduction of these species which are nearby but what we will be seeing overall that if you have all these are in the solution, so those species whether it is the species which is the responsible for reduction or the species responsible for oxidation, which are nearby to that of your electrode are giving that particular reaction very quickly.

But those are here but those are here they have to cross this particular concentration gradient and from the solution basically because this is the solution to you have to go to the electrode surface which is very important. Therefore you have some interfacial region and these interfacial regions are very small and it can be fraction of some nanometres. So fraction of nanometre and we are looking for that means the species that means the analyte that means the reactant, how quickly the reactant are reaching the electrode then means mass is being transported that means we are talking something related as a concentration gradient is there, therefore we have to talk about the corresponding mass transfer.

So the mass transfer process is therefore is there and the reaching of reactant to the electrode surface that means the transportation of the reactant is dependent on several factors like 1, 2 or 3 we can consider right now. One is your diffusion, second one is the migration and third one is convection, so these are the things which are responsible for transferring the thing that you can go for the transfer of your species for solution to the electrode surface and that is therefore very much important then the second one.

One was concentration and the second one is your kinetic one, so kinetic one is also related to that of your current that the magnitude of current what is getting so is basically related to the corresponding limiting thing and where we get the rate of one or both the electrodes reactions that means it is dependent on the electrode reactions and those electrodes reactions you have over voltage and how to overcome that means if you have over voltage so you have to overcome that over voltage.

To overcome that thing we have to go for that that means the activation energy to be considered and that activation energy when we consider for this thing that that activation energy is therefore the corresponding barrier for the different half reactions without the half cell reactions for those electrodes. So we will see these things are together very much important for controlling the corresponding reaction whether we go for any electrogavimetric technique or which can be a control potential or sometime it cannot be controlled by the potential controlling mechanism.

So the diffusion that means the when is diffusion is there that means there is a concentration gradient and that particular concentration gradient is basically disappearing so what diffusion is telling us that disappearance of the corresponding concentration gradient so that means diffusion is if it is operating so we do not find any kind of cell concentration polarization. So disappearance of the concentration gradient is there. Then for migration we must have electrostatic attraction between the ions and the electrodes that means electrostatic are working and between the ions and the electrodes.

So this is important that if there is some interactions because ions are charged and electrodes are also charged so if there is some attraction so migration will be facilitated and convection we just simply allow by doing this by using a magnetic stirrer so mechanical means of stirring is useful so stirring is there, so that will allow the convection which will remove the concentration gradient and also we have seen that we can use the addition of supporting electrolyte.

So addition of supporting electrolyte reduces the cell potential and that supporting electrolyte that means supporting electrolyte also decreases or reduces the IR drop. So these things that means which are going against the corresponding measurement or the current transfer or the passage of the current should we should keep in our mind that there should be some corresponding current has diffusion control current we will call then migration and then convection how we can use so when we see the actual practise of all these things, we will see and we will discuss once again that how and why and what sort or supporting electrolyte we can use such that we can decrease the corresponding IR drop within the cell, Thank you very much